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COMPLETE SPECIFICATION

Fuel Oil Additive

We, CANADIAN PATENTS AND DEVELOPMENT LIMITED, a company duly incorporated under the laws of Canada to which the Government Companies Operation Act applies, and having its head office at National Research Building, Montreal Road, Ottawa 7, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to fuel oil additives. The invention seeks to provide a fuel oil additive which is intended to reduce slagging in the tubes of industrial and the like oil-fired boilers, to facilitate the removal of slag and like deposits from the fireside of such boiler tubes, to reduce acid smut pollution (acid smut is defined as carbon soot that has adsorbed SO_3 and becomes corrosive when cooled below acid dewpoint temperature that may range from 350°F. to 140°F.), to eliminate low temperature corrosion, and to improve the electrical resistivity of particulate emission from a fuel oil flame.

The use of fuel additives to prevent slag build-up, corrosion of both high and low-temperature heat transfer surfaces and the like in coal and oil fired boilers has been the subject of a great deal of research since, for satisfactory operation of the boiler, it is essential that the boiler tubes be kept substantially free of slag build-up and corrosion products.

Such research has resulted in many proposals for solution of the problem. United States Patent 3,002,826 proposes use of an additive in the form of an emulsion, the water phase of which is an aqueous solution of a salt of Al, B, Cu, Si or Zn, and the oil phase of which is a mineral oil. United States Patent 3,004,836 relates to the use of a ground magnesia-phosphate mixture for preventing slag build-up in coal-fired boilers. United States Patent 3,036,901 proposes the use of a finely divided, oil-insoluble, metallic additive which is initially suspended in a hydrated calcium acetate gel before being blended with a residual fuel oil carrier. United States Patent 2,845,338 proposes use of an additive comprising a mixture of a magnesium compound and a compound of Cu, Co, Mn, Fe or Ca. United States Patent 3,067,018, relates to use of a specially formed emulsion of an oxide, hydroxide or carbonate of the metals of group II of the periodic system.

According to the present invention, there is provided a fuel oil additive which comprises a dispersion of finely divided particles of partially dehydrated hydroxides of magnesium and aluminium in a petroleum oil containing one or more anionic or non-ionic surfactants, the weight ratio of magnesium: aluminium being at least 1:1, said hydroxides having a minimum bound water content of 0.5% by weight and a maximum bound water content of 15% by weight.

The surfactant is included in order to convert the dispersion into a free-flowing, easily pumpable suspension.

The magnesium and aluminium active ingredients may be denoted as $MgO \cdot xH_2O$ and $Al_2O_3 \cdot yH_2O$, respectively, where $x<1$ and $y<3$. These partially dehydrated hydroxides may also be described as a compound mixture of oxides and hydroxides having the general formulae

$$Mg_{II}O \cdot OH \text{ and } Al_{III}O \cdot OH.$$

The elemental magnesium present in the additive is not less than the amount of ele-

mental aluminium in the additive. The hydroxides contain from 0.5 to 15%, preferably 0.5 to 5%, by weight of bound water. A satisfactory weight ratio of magnesium: aluminium for most industrial applications is from 1:1 to 10:1.

The partially dehydrated hydroxide particles, which preferably range from 1 to 7 microns in size, are predominantly granular in shape to prevent erosion and plugging of fuel oil handling and atomizing equipment. The partially dehydrated hydroxide of magnesium is preferably obtained from sea or salt water because of its low abrasiveness and high chemical reactivity. The preferred particle size range mentioned above acts to control the physical structure as well as the quantity of material that deposits in both hot and cold regions of the boiler. The particles preferably have high specific surface areas varying from 400 to 1400 square metres per gram to maximize chemical reaction with combustion residues in gas, vapour and liquid state. The diameter of the pores permeating each particle should preferably range from 17 to 20 Angstroms for optimum physical adsoprtion of gas-phase pollutants.

The petroleum oil, which acts a carrier, is preferably a light hydrocarbon oil having a maximum viscosity of 35 SSU at 100°F.

The surfactants is anionic or non-ionic and must be compatible with the active ingredients and with the petroleum oil. It transforms the highly viscous, two-phase mixture into a free-flowing easily pumpable suspension that blends readily with fuel oil. Suitable surfactants are readily available. For example, the glycerol stearates and laurates and the heavy metal soaps of stearic, naphthenic and rosin acid, are particularly suitable. Examples of specific surfactants are glycerol monostearate (as sold under the trade name "ALDO 33" by Glycol Products Company); lecithin (as sold under the trade name "CLEARATE" by W. A. Cleary Corporation); sorbitan monolaurate, sorbitan tristearate, and glycerol sorbitan laurate (as sold under the trade names "SPAN 20", "SPAN 65", and "G-672", respectively, by Atlas Powder Company; the word "SPAN" is a Registered Trade Mark); and heavy metal soaps, such as aluminium stearate, produced by reaction of a water soluble soap with a heavy metal salt of aluminium, magnesium, cobalt, zinc, manganese or calcium.

An example of a mixture of surfactants that can be used in the additive of the invention is a mixture of a predominantly water-soluble dispersant, as sold under the trade name "TIC" by Dowell Canada Limited, and a predominantly oil-soluble lanolin derivative, as sold under the trade name "POLYAN" by American Chloresterol Products Inc.

A single surfactant which exhibits both water- and oil-soluble characteristics can be used to produce an additive having reasonably good fluidity, stability and blending properties. Examples of such surfactants are the sodium methyl laurates as sold under the name "IGEPON" by General Aniline and Chemical Corporation, the ethoxylated nonyl phenols are sold under the Registered Trade Mark "RENEX" by Atlas Chemical Industries, and a polyhydroxy alcohol-fatty acid ester as sold under the Registered Trade Mark "TENLO 68-S" by Nopco Chemical Company.

These surfactants also disperse and stabilize the solids in suspension by eliminating attractive forces on the particle surfaces. The surfactant is preferably in concentrations of from 0.7% to 3.5% by weight, more preferably about 2.0%.

The additive of the invention is a stable suspension preferably containing 40—60% by weight of the hydroxides and preferably having a viscosity of less than 115 SSU at 80°F. Other preferred physical characteristics are:

Specific Gravity at 70°F.	=1.35
Flash Point (PM), °F.	=150 minimum
Pour Point, °F.	=−10 maximum

Alleviation of High Temperature Deposits and Corrosion

Laboratory experiments, using a combustion rig closely simulating field conditions, have shown that the additive described is particularly effective in changing the normally rock-like fuel ash slag into a porous, friable, powdery deposit that is easily removed by routine soot-blowing procedures. The deposit build-up with use of the additive is loosely bonded to boiler tube surfaces and weakly agglomerated.

The deposits produced when using the additive were subjected to an intensive thin section investigation to clarify the role of additive properties, such as mineral composition and physical state, in preventing slag formation. Microscopic examinations of deposit thin sections showed a thin, dense, unsintered layer of sub-micron particles next to the tube surfaces. Subsequent deposits formed an intermediate upstream layer of friable, moderately porous material, an outer upstream layer having a thick, porous, wedge-shaped structure and an outer downstream layer of powdery, moderately porous, lightly sintered crystals.

By optical and X-ray diffraction methods, it was determined that a magnesia-alumina reaction product, known as spinel was uniformly distributed throughout all four layers and that the proportion of magnesium sulphate to magnesium oxide increased progressively toward the tube surface. The work also revealed that most of the vanadium was concentrated in the intermediate upstream and the outer downstream layers as bands of sodium vanadyl vanadate and magnesium

orthovanadate. The partially dehydrated magnesium hydroxide component, therefore, prevents slagging of low-melting sodium and vanadium compounds by both mechanical dilution and chemical reaction.

The partially dehydrated aluminium hydroxide component also plays two important roles in modifying the slag structure. First, alumina, by reacting selectively with magnesia in the flame to form spinel, reduces the magnesium available for later reaction with sulphur oxides on the tube surface; this dictates the elemental magnesium to aluminium ratio for particular combustion conditions. The formation of magnesium sulphate, which is molten and sticky at 2050°F. should be minimized, particularly when gas temperatures at the furnace exit are above 2100°F.; this is accomplished by increasing the aluminium active ingredient in the additive. Second, the magnesia-alumina reaction product reduces the tendency of unreacted but superfine magnesia particles to agglomerate. This control over agglomeration is probably due to the presence of uniformly distributed spinel particles that form cubic crystals of octahedral shape.

Porosity measurements on deposit samples also revealed that high porosity and large voids were specific to partially dehydrated hydroxides of magnesium and aluminium having particle sizes ranging from about 1 to about 7 microns. Control of particle size is important because theoretical studies showed that particles larger than 10 microns tend to form undesirable, densely impacted deposits. On the other hand, particles less than 0.5 microns tend to form undesirable cohesive deposits having small voids.

The additive of the present invention is thus suitable for controlling slag deposits on boiler surfaces over a wide range of gas temperatures. Furthermore, by preventing slag formation on tube surfaces, high temperature oil ash corrosion becomes impossible so that tube temperatures may be safely maintained at 1100°F.

To supplement the laboratory research, two power utility companies conducted field trials with additives of the invention. In both cases the boils involved were rated at 360,000 lb/hr of steam at 900 psig and 900°F

Previously, these boilers were plagued with expensive maintenance and repair costs due to slagging and blocking of superheater elements every 4 to 6 weeks. Several proprietary anti-slagging additives had been tried during a four-year period but all were expensive and ineffective.

The oil-base additive employed in the full-scale trials was used at a dosage rate of 1 gallon of additive per 1500 gallons of fuel oil, and had the folowing specific formula and characteristics: —

Magnesium: Aluminium—element weight ratio	10:1
Particle Size Range, μ	1—7
Specific Gravity at 70°F.	1.35
Flash Point, (PM), °F	150
Pour Point, °F.	−10
Solids Content, % by weight	48

After four weeks of operation with this additive (a) the hard, bonded slag build-up was replaced with a soft, friable powder that was easily removed by soot blowing, (b) bridging in the convection pass of the generating bank was eliminated, and (c) a light coating of additive oxides on the furnace walls was credited with raising superheat temperatures to design conditions for the first time.

A shipboard trial has also been made with an additive as described above but with a magnesium to aluminium ratio of less than 2:1.

The ship's boilers being used for this trial suffered from severe superheated slagging because of their stringent design conditions. Typical boiler operating data are:

(a) 2500°F. gas temperature at the superheater,

(b) 975°F. superheater tube temperature, and

(c) 500 psig steam pressure from 5% to 125% of rated steam flow.

This trial is being conducted with an additive dosage rate of 1 gallon per 1000 gallons of fuel oil and information, supported with photographs, received from the ship indicates that superheater slagging has been successfully suppressed.

From results of the aforementioned laboratory experiments and field trials, it is concluded that the following additives and dosage rates are effective in preventing deposition and corrosion due to molten oil-ash constituents:

Furnace Exit Temperature, °F.	Additive Mg/Al Ratio	Additive Dosage Rate gal/gal
1850 or less	10:1	1:1800
1850—2501	5:1	1:1500
2150—2450	3:1	1:1200
2450 or over	<2:1	1:1000

Control of Low Temperature Deposits and Corrosion

Laboratory combustion rig experiments have been conducted with the following oil-base additive:

Magnesium: Aluminium—element wt. ratio	2:1
Particle Size Range, μ	1—7
Specific Gravity at 70°F.	1.35
Flash Point (PM), °F.	150
Pour Point, °F.	—10
Solids Content, % by wt.	48

These experiments have demonstrated that the fuel-oil additive of the invention reduced sulphuric acid corrosion on low-temperature boiler surfaces by 35% to 66% depending on the additive dosage rate. Laboratory studies have also indicated that a thin, uniform layer of active ingredients deposits on cold end surfaces by a process of agglomeration where they soak up and react with any condensed acid. The residue, after reaction with acid, consists mostly of water-soluble, non-toxic hydrated magnesium and aluminium sulphates that area easily removed by brushing or water-washing.

In related laboratory research experiments, it has been established that time-temperature conditions in industrial flames are not severe enough to dehydrate the active ingredients completely. Furthermore, partial rehydration between the magnesium active ingredient and water vapour in the flue gases occurs in the low-temperature region of the boiler. This rehydration phenomenon, by replacing evaporated hydroxyl groups, enhances the chemically basic properties of the magnesium active ingredient. The partially dehydrated hydroxides of aluminium, even if further dehydration occurs in the flame, will react with acid. However, it is important to note that the use of aluminium active ingredient derived from crystalline or other forms of alumina (Al_2O_3) which do not contain bound water is avoided because acid neutralization reactions do not occur.

Field trials have also been conducted, using the following oil-base additive:

Magnesium: Aluminium—element weight ratio	10:1
Particle size range, μ	1—7
Specific Gravity at 70°F.	1.35
Flash Point (PM), °F.	150
Pour Point, °F.	—10
Solids Content, % by weight	60

These trials were conducted in a number of power utility boilers that experienced serious cold and fouling and corrosion problems. In all trials the additive was initially applied at the rate of 1 gallon per 1500 gallons of fuel oil, after which the dosage rate was gradually reduced to 1 in 1800.

At the end of 8 weeks operation with additive-treated oil, the draft loss across the air heater of each boiler was unchanged, this indicated that frequent and periodic plugging of the tubular air heaters was no longer a problem. Inspection of the air heaters revealed that the active additive ingredients had completely dried up the original gummy, corrosive cold end deposits and that the thin coating of additive material on the tube surface was loose and powdery.

The boilers, which are now operating regularly on additive-treated fuel oil, no longer require soot-blowing in the air heater zone and regular bi-monthly boiler outages for cleaning and replacement of air heater elements have been eliminated. The extremely low rate of increase in draft loss across the air heaters of these boilers indicates that cleaning of fireside surfaces can be programmed to coincide with annular boiler maintenance.

In one field trial the use of an oil-base additive of the invention having a magnesium to aluminium ratio of 10 to 1 resulted in a 90% reduction of SO_3 in the stack gases when applied at the rate of 1 gallon per 1800 gallons of fuel oil. During this trial, SO_3 levels were reduced from 30 ppm to 3 ppm and the white acid plume from the stack was eliminated.

To complement the findings of the aforementioned field trials, an additive of the invention was evaluated in a pilot-scale research boiler. It was found that the additive, which had an elemental magnesium to aluminium ratio of 10 to 1, was effective in (a) reducing SO_3 levels by about 80%, (b) reducing oxides of nitrogen levels by about 20%, and (c) preventing the formation of gummy, corrosive low-temperature deposits when applied at the rate of 1 gallon per 1500 gallons of fuel oil.

Abatement of Acid Smut Emission

Another benefit from using the fuel-oil additive invention has been the abatement of acid smut emission. Without using the additive, acid smut, or soot soaked with sulphuric acid normally builds up in the cold end of a boiler or process and on the stack lining to some equilibrium thickness, after which it suddenly breaks free. Following emission to atmosphere these corrosive, sticky flakes of acid smut fall on people and property creating a serious nuisance problem and, in some cases, considerable damage to fabrics, crops and automobile finishes.

In large oil-fired boilers, exit gas temperatures often fall below the acid dewpoint. When this occurs and the additive is not used, electrostatic precipitators must be by-passed because of the potential fire hazard from the wet, combustible acid smut that is usually present. In such cases, smut emission is par-

ticularly bad, atmospheric pollution ordinances are frequently violated, and many complaints are commonplace.

This problem was eliminated entirely in one power utility boiler by applying the oil-base additive having an elemental magnesium to aluminium ratio of 10 to 1 at the rate of 1 gallon per 1500 gallons of fuel oil. Furthermore, the electrical resistivity of the solid residues leaving the boiler was improved to the extent that particulate matter could be collected by the electrostatic precipitators. This solid residue, being dry and powdery, was also easily removed from boiler and dust collector hoppers. The same beneficial results were obtained in a pilot-scale research boiler by applying an oil-base additive of the invention having an elemental magnesium to aluminium ratio of 10 to 1, at the rate of 1 gallon per 1500 gallons of fuel oil.

In another power utility boiler the oil-base additive having an elemental magnesium to aluminium ratio of 10:1 was applied at the rate of 1 gallon per 1500 gallons of fuel oil for the purpose of controlling acid smut pollution and low temperature corrosion. Reports on the results of this trial state: " The effect of the chemical's use are visible, both from a distance and at the stations themselves. Most days the air above the stacks is free of what used to be the normal dark plume, and the area around the stations is practically free of fly ash fall-out. Even more important to the generating station operators, the soot and slag no longer clog up the huge air heaters connected to the furnaces. Normally, those units, which heat the air that's used in the boiler for combustion purposes, had to be washed out every six weeks ".

The fuel-oil additive described herein provides an economic means of controlling or eliminating boiler operational problems due to incombustible constituents in residual fuel oil. Economic benefits from using the additive include increased boiler availability and efficiency, reduced maintenance and fuel costs, and, in some cases, a financial credit on the sale of vanadium-rich ash collected in boiler and dust colelctor hopeprs. Another major, but less tangible benefit, is the favourable public image created by minimizing the emission of noxious atmospheric pollutants.

The additive, which is normally metered continuously and automatically into the oil supply to each burner, can be formulated to the specific requirements of a particular boiler. Additive dosage rates will vary according to fuel analysis and combustion conditions, but usually 1 gallon per 1500 gallons of fuel oil is sufficient to control most problems at the cold end of a boiler or the like.

The additive of the present invention is thus effective in

(a) alleviating high temperature slagging and corrosion,
(b) neutralizing and drying up gummy corrosive deposits at the cold end of a boiler,
(c) reducing the level of SO_3 and nitrogen oxides in flue gases,
(d) preventing the formation of acid soot, and
(e) making it possible to control the emission of soot to the atmosphere.

WHAT WE CLAIM IS:—

1. A fuel oil additive which comprises a dispersion of finely divided particles of partially dehydrated hydroxides of magnesium and aluminium in a petroleum oil containing one or more anionic or non-ionic surfactants, the weight ratio of magnesium: aluminium being at least 1:1, said hydroxides having a minimum bound water content of 0.5% by weight and a maximum bound water content of 15% by weight.

2. An additive as claimed in Claim 1, in which the particles have a size of from 1 to 7 microns.

3. An additive as claimed in Claim 1 or 2, in which the dispersion has a solids content of from 40 to 60% by weight.

4. An additive as claimed in any of the preceding claims, in which the dispersion has a maximum Saybolt viscosity of 115 universal seconds at 80°F.

5. An additive as claimed in any one of the preceding claims, in which the amount of elemental magnesium in the dispersion is greater than the amount of elemental aluminium in the dispersion.

6. An additive as claimed in any one of the preceding claims, in which the petroleum oil has a maximum Saybolt viscosity of 35 universal seconds at 100°F.

7. An additive as claimed in any one of the preceding claims, in which the surfactant is present in an amount of from 0.7 to 3.5% by weight.

8. An additive as claimed in any one of the preceding claims, in which the surfactant is a glycerol stearate or laurate, lecithin, a fatty acid, or a heavy metal soap or stearic, naphthenic or rosin acids.

9. An additive as claimed in any one of the preceding claims, in which the particles have a specific surface area of from 400 to 1400 square metres per gram.

10. An additive as claimed in any one of the preceding claims, in which the particles are porous, the diameter of each pore of the particles being at least 17 Angstrom units.

11. An additive as claimed in Claim 10, in which the diameter of each pore of the particles is from 17 to 20 Angstrom units.

12. An additive as claimed in any of the preceding claims, in which the particles have from 0.5 to 5% by weight of bound water.

13. An additive as claimed in any one of the preceding claims, in which the ratio of the elemental magnesium: aluminium is less than 10:1.

14. A fuel oil additive in accordance with Claim 1, substantially as hereinbefore described.

15. A method of preventing oil ash slagging, low temperature corrosion, acid smut emission, of reducing the level of SO_3 and nitrogen oxides in flue gases, and of chemically neutralizing and drying-up gummy, corrosive deposits that form below acid dewpoint temperatures, in oil fired boiler systems and the like, which comprises adding a fuel oil additive as claimed in any one of the preceding claims to the fuel oil in an amount of one part by volume of additive to each 1000 to 2000 parts by volume of fuel oil.

16. A method in accordance with Claim 15, substantially as hereinbefore described.

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